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Concept of Covalent and Polar Nature in Chemical Bonds and Its Application to Radical Reaction

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The electronic theory of organic chemistry established by Robinson-Ingold has long been developed by Hammett, Price and others. In contrast with this classical approach the theoretical organic chemistry based on quantum chemistry seems to be more promising but at the present stage the latter is not always valid similarly as the former. In the field of non-conjugated and heteroatomic system the classical theory is still important, although it has strictly no theoretical background. The author's *J-e* concept, which belongs to the classical one, may contribute to some extent in this field.

INTRODUCTION

In organic chemistry radical reaction affords a new research field besides ordinary ionic reactions, for example polymerization of vinyl and olefinic compounds is one of the most useful reactions. It is desirable to find out a general rule to interpret radical reactions similarly to the Hammett rule which holds good for ionic reaction.

In polymerization reaction the well known scheme was proposed by Price-Alfrey, which consists of Q and e values representing the reactivity factor and the polar nature of monomers in co-polymerization, respectively. This article attempts to derive a similar relation from other physical properties such as bond dissociation energy and to apply it to radical reactions.

I. EMPIRICAL CALCULATION OF CO-VALENT AND POLAR NATURE OF RADICALS FROM BOND ENERGY DATA

Bond dissociation energy implies the free energy required for homolytic dissociation of chemical bond and bond energy is that of the reverse process. Both of them concern the nature of two components of which the bond consists. Usually it may be reasonable that the bond consists of component or radical of great activity and the sum of reactivities of both radicals may roughly represent the bond energy consisting of corresponding radicals. However for precise examination of bond energies the additional term is necessary. If the bond is composed of polar radicals, the following expression is proved to be suitable for the heteropolar bond[1].

$$D_{AB}=J_A+J_B-e_Ae_B, \qquad (1)$$

where D_{AB} is the bond energy for the bond AB and J and e are characteristic

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Table 1. Bond energies and

	H·	CH_3·	C_2H_5·	CH_2=CH·	CH≡C·	$_nC_3H_7$·	$_tC_3H_7$·	CH_2=CH·CH_2·	ϕ·	ϕCH_2·	$_nC_4H_9$·	$_tC_4H_9$·
J	56	41.5	41.5	50	69	39	34	20	54	23	34	30
e	+2.8	0	0	0	?	0	0	0	+2	0	0	−0.2
H·	(104) 104	(97.5) 101	(97.5) 98	(116) 104?	(125) 121?	(95) 95	(90) 89?	(76) 77	(104) 104?	(74) 77.5	(90) 94	(87) 85?
CH_3·	(97) 101	(83) 83	(83) 82	(91) 90?	(110) 110?	(80) 79	(75) 74.5	(61) 60	(89) 94	(64) 63	(76) 78	(73) 74?
C_2H_5·	97	82	(83) 82	(91) 90?	(110) 109?	(80) 79	(75) 75?	(61) 60.5	(90) 94?	(64) 62	(76) 78	(73) 73?
CH_2=CH·	104?	90?	90?	(100) 104?		(89) 87?	(84) 85?	(70) 68.5?	(104) 104?	(73) 101?	(84) 86?	(80) 81?
CH≡C·	121?	110?	109?			(108) 106?	(103) 103?		(121) 119?			
$_nC_3H_7$·	95	79	79	87?	106?	(78) 76	(73) 72?	(57) 57.5	(62) 88?	(52) 59		
$_tC_3H_7$·	89?	74.5?	75?	85?	103?	72?	(68) 66.5	(54) 54.5?	(87) 83?			
CH_2=CH·CH_2·	77	60	60.5	68.5?		57.5	54.5?	(40) 38				
ϕ·	104?	94?	94?	101?	110?	88?	83?		(104) 103?			
ϕ·CH_2·	77	63	62	101?		59	54.5?		76.5?			
$_nC_4H_9$·	94	78	78	86?		75	71?	56.5	87?			
$(CH_3)_2CH$·	89?											
$_tC_4H_9$·		74?	73?	81?		70?	65?		78?			
·Cl		80	80	86?		77		58	88?			75?
·Br		66	65	8±4				48		50.5		61?
·I		54	51	55?		50	~46	36	57?	39?		~45?
·OH	115~ 118	90,91	90,93	91?		92	~90	71	107?	73		
·NH_2	124~ 104	79	78			77		64?	94?	59		76?
·CN	121?	110?		121?				92?	124?	95?		
·CHO		71~75	71?	84?			71?	50?	83?			
CH_3CO·		77?	77?				77?			63		73?
·NO_2		57	52									
·NO												
·SH		74.2	73.5			72.1	70.6	54.3				69.4
·SCH_3	>78?	73.2	71.8			69.7	67.0	51.9				65.2
SC_2H_5		70.6	69.3			67.7	65.2	49.9				62.2

* Franklin, Lampkin, J. A. C. S., **74** 1023, (1952). ** Szwarc, Chem. Rev., **47**, 75~173 (1952).

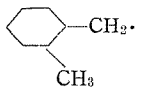
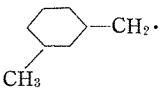
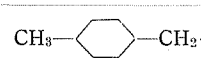
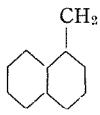
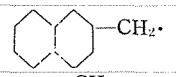
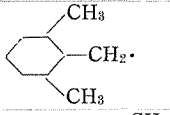
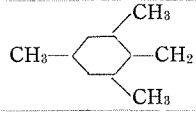
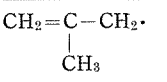
their calculated values.

(kcals/mole, J in kcals/mole, e in (kcal) 1/2)

·CHO	$CH_3\dot{C}O$	·Cl	·Br	·I	·OH	·NH_2	·CN	·NO_2	·NO	·SH	·SCH_3	·SC_2H_5	$\overset{*}{C_5}\overset{**}{H_5}\dot{C}O$
33.5	35	32	25	15	46	44	63	12	2?	30	30	27	30.7
+3.3	+3.3	−2	−0.3	+1	−6	−5.2	−2.5	+1	0	0?	0	0	+2.5
(79) 78					(120) 115∼118	(125) 124∼164	(127) 121?			(86) 78?			(79.7) 78.8
(75) 75	(76) 77	(73.5) 74	(76) 66	(56.5) 54	(88) 90,91	(85) 79	(105) 105	(54) 57		(72) 74.2	(72) 73.2	(69) 70.6	(72.2) 71.7
(75) 71	(76) 77?	(72) 80?	(76) 65	(56.5) 51	(88) 90,93	(85) 78		(54) 52		(72) 73.5	(72) 71.8	(69) 69.3	
(87) 84		(82) 86?	8?	(68) 55	(96) 91?		(113) 121?						
		(71) 77		(54) 50	(85) 92	(83) 77				(69) 72.1	(69) 69·6	(66) 67.7	
(67.5) 71	(69) 77?			(45) 46	(79) 90					(64) 70.6	(64) 67.0	(61) 65.2	
(53) 50		(52) 58	(45.5) 45,48, 50	(35) 36	(66) 71	(64) 64?	(83) 92			(50) 54.3	(50) 51.9	(49) 49.9	
(82) 83		(87) 88		(67) 57?	(95) 107	(103) 94?	(119) 124?						
(58.5) 63	(58) 63		(46) 50.5	(38) 39?	(69) 73	(63) 59	(88) 95?						
	(66) 73?	(62) 75?	(55) 61?	(45) 45		(75) 76?				(60) 69.4	(60) 65.2	(57) 62.2	
(79) 79?	(75) 85?	(60) 56.9					(90) 95?		(34) 37				(67.7) 73.5
	(59) 67?		(50) 45.2				(87.5) 83?		(27) 28				(56.5) 57
	(47) 51?			(29) 31.6			(71) 71?						(43.2) 42.4
96?	(101) 102?				(56) 54								(91.7) 93.6
(85) 89?	(95) 98?					(60) 60±4							(87.7) 86.6
		(90) 95?	(77) 83?	(80) 71?			(120) 100∼ 140						
	59?												
(59) 59?	(60) 60	(83.5) 85			−90?								
								(14) 14	(14) 10				
		37	28					(15) 10					

*** Ladachi, Leigh, Szwarc, J. Proc. Royal Soc., **214**, 278 (1952).

Table 2. J and e

Radical	J	e	Radical	J	e	Bond energy
H·	56	42.7		34(?)	0	$D_R-H=34(?)$
CH_3·	41.5	0	$C_6H_5CH_2CH_2$·	<32	0	$D_R-H=47$
C_2H_5·	41.5	0	$(C_6H_5)_2CH$·	5(?)	0	$D_RC(CH_3)_3=28$
$_nC_3H_7$·	39	0	$(C_6H_5)_3C$·	19	0	$D_R-H=75$
$_tC_3H_7$·	34	0		19	0	$D_R-H=75$
$_nC_4H_9$·	34	0				
$_tC_4H_9$·	30	−0.2				
$CH_2=CH$·	50	0		21	0	$D_R-H=77$
CH≡C·	63	?				
$CH_2=CH\cdot CH_2$·	20	0		20	0	$D_R-H=76$
C_6H_5·	54	+2				
$C_6H_5CH_2$·	23	0		20	0	$D_R-H=76$
·CHO	33.5	+3.3				
CH_3CO·	35	+3.3				
·Cl	32	−2		20	0	$D_R-H=76$
·Br	25	−0.3				
·I	15	+1		11	0	$D_{R^2}=22$
·OH	46	−6				
$\cdot NH_2$	44	−5.2		11	0	$D_{R^2}=22$
·CN	63	−2.5				
$\cdot NO_2$	12	+1				
·NO	2(?)	0		20	0	$D_R-H=76$
·SH	30	0(?)				
C_6H_5CO·	30.7	+2.5				

factors referred to radical components A and B.

Subsequent study will make it clear that J and e represent covalent bonding activity and polar activity of radicals, respectively. J_A and e_A can be calculated from various bond energies concernig radical A by using the following equations

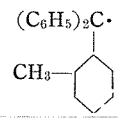
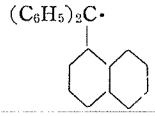
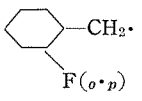
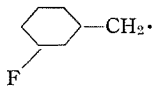
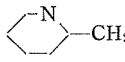
$$D_{AA}=2J_A-e_A^2$$

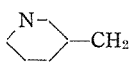
$$D_{BB}=2J_B-e_B^2$$

$$(e_A-e_B)^2=2J_B-e_B^2.$$

Table 1 summarizes calculated values of J and e of various radicals. The comparison of calculated bond energies expressed in parenthesis with the observed value implies the validity of J-e scheme. From experience of organic chemistry, J values seem to express the reactivities of free radicals concerned, which decreases according to the J-value, while e-values seem to agree with their polar natures as listed in Table 2.

values of radicals.

Radical	J	e	Bond energy
	5.7	0	$D_{R2}=11.4$
	5.7	0	$D_{R2}=11.5$
$BrCH_2\cdot$	43	0	$D_R-H=99$
$Cl_2CH\cdot$	27	0	$D_R-H=42$
$Br_2CH\cdot$	27	0	$D_R-H=41$
$I_2CH\cdot$	22	0	$D_R-H=22$
$Cl_3C\cdot$	33	0	$D_R-H=89$
$Br_3C\cdot$	37	0	$D_R-H=37$
$F_3C\cdot$	35	0	$D_R-I=5\sim57$
$ClCH_2CH_2\cdot$	31	0	$D_R-I=46?$
$ICH_2CH_2\cdot$	32	0	$D_R-H<47$
	26	0	$D_R-H=51$
	22	0	$D_R-H=78$
	22	0	$D_R-H=78$
	19	0	$D_R-H=75$

Radical	J	e	Bond energy
	20	0	$D_R-H=76$
	21	0	$D_R-H=77$
$C_6H_5NH\cdot$	29	−5	$D_R-NH_2\sim48$ $D_{R2}\sim35$
$(CH_3)_2N\cdot$	9	−5(?)	$D_R-CH_3=50.8$
$(CH_3)NH\cdot$	10	−5(?)	$D_R-CH_3=52.0$
$CH_3O\cdot$	40	0(?)	$D_R-CH_3=81.8$ $D_R-COCH_3=74.2$
$C_2H_5O\cdot$	27	−5	$D_{R2}=30$ $D_R-C_2H_3=68.6$
$C_8H_7O\cdot$	27	3(?)	$D_R=35$
$(CH_3)_3CO\cdot$	27	3(?)	$D_{R2}=34\sim39$
$CH_3S\cdot$	30	0(?)	
$C_2H_5S\cdot$	27	0(?)	
$C_6H_5COO\cdot$	—	—	$D_X=\sim30$
$CH_3COO\cdot$	—	—	$D_X=\sim30$

In fact radicals of high J-value such as H·, $CH_3\cdot$, $C_6H_5\cdot$ and OH· are usually very reactive as usual and that of low J-value such as I·, $No_2\cdot$ and No· are stable. Further large electrophilic properties of H· and $C_6H_5\cdot$, and large nucleophilic ones of $\cdot NH_2$, $C_2H_5O\cdot$ and ·OH seem to correspond to their large e-values.

As to bond energies of heteroatomic bond other than organic bonds the similar expressions are possible as summarized in Table 3, where average bond energies are expressed.

II. RELATION BETWEEN SEVERAL EQUATIONS OF BOND ENERGIES

About bond dissociation energies Pauling[2] has already pointed out that bond dissociation energy of hetero-bond is always larger than that of homopolar one and he proposed the following expression,

$$D_{AB}=(D_{AA}+D_{BB})/2+\Delta, \qquad (2)$$

Bond Energies and Reactivity of Radicals. (I)

Table 3. Average bond energy of atoms in kcal/mole

H	C	N	O	F	Si	P	S	Cl	Ge	As	Se	Br	I			
53	29	17	41	78	36	17	30	37	44	10	36	25	17	J		
+2.8	0	−3.5	−7	−9.6	+3.9	+2.8	0	−4	+6	+5	+2	−1.85	0	e	J	
(98) 103.4	(82) 87.3	(80) 83.7	(113) 110.2	(158) 147.5	(79) 75.1	(62) 63.0	(83) 87.5	(102) 102.7	(80)	(49)	(83)	(83) 87.3	(70) 71.4	+2.8	53	H
	(58) 58.6	(46) 48.6	(70) 70.0	(107) 107.0	(65) 57.6	(46)	(59) 54.5	(66) 66.5	(73)	(39)	(65)	(54) 54.0	(46) 45.9	0	29	C
		(22) 20.2	(34) —	(62) 68.8	(66) —	(44)	(47)	(40) 38.4	(82)	(44)	(60)	(35)	(34)	−3.5	17	N
			(33) 34.9	(52) 58.6	(102) 89.3	(78)	(71)	(50) 49.3	(127)	(86)	(91)	(53)	(58)	−7	41	O
				(64) 63.5	(148) 143.0	(122)	(108)	(77) 86.4	(179)	(136)	(133)	(85)	(95)	−9.6	78	F
					(58) 42.5	(42)	(66) 69.9	(89) 85.8	(57)	(27)	(64)	(68) 69.3	(53) 51.1	+3.9	36	Si
						(26) 18.9	(47)	(65) 62.8	(44)	(13)	(47)	(47) 49.2	(34) 35.2	+2.8	17	P
							(60) 66.8	(67) 66.1	(74)	(40)	(66)	(55) 57.2	(47)	0	30	S
								(58) 57.5	(105) 104.1	(67) 60.3	(81) 66.8	(55) 57.2	(54) 51.0	−4	37	Cl
									(52) 42.5	(24)	(58)	(80)	(63)	+6	44	Ge
										×(−5) 15.1	(36)	(44) 48.0	(27) 33.1	+5	10	As
											(68) 57.6	(65)	(53)	+2	36	Se
												(47) 46.1	(42) 42.9	−1.85	25	Br
													(34) 36.2	0	17	I

where D_{AA} and D_{BB} are both homopolar bonds of AA and BB, respectively, and Δ is the exaltation value from mean value of bonds AA and BB due to the ionic contribution of bond AB, which was predicted to be proportional to the square of the difference of electronegativity values, X_A and X_B, of both atoms A and B, as is expressed by the following equation (3):

$$D_{AB}=(D_{AA}+D_{BB})/2+23.06\ (X_A-X_B)^2 \qquad (3)$$

The equation (2) can be recognized essentially to be the same as equation (3), if eq.

(3) is expanded and arranged into such an equation as (4).

$$D_{AB}=D_{AA}/_2+23.06\ X_A^2)+(D_{BB}/2+23.06\ X_B^2)-46\ X_AX_B \qquad (4)$$

Equation (4) involves three terms, two of which relate to atom A or B alone and the third one to both A and B. Therefore it follows that

$$\begin{aligned} J_A &= D_{AA}/2+23.06\ X_A^2 \\ J_B &= D_{BB}/2+23.06\ X_B^2 \\ e_A &= \sqrt{46}\ X_A \\ e_B &= \sqrt{46}\ X_B. \end{aligned} \qquad (5)$$

There has long been known Hammett's rule for the reaction rate of aromatic compound, while Price-Alfrey equation for co-polymerization. These equations are similar in form to equation (4) and the correlation among them will be discussed in the following sections.

III. INTERPRETATION OF RADICAL REACTION IN TERMS OF $J-e$ SCHEME

The free radical type reactions are considered to be much more complicated than usual ionic ones and it is one of the most difficult problems to discuss on the reactivity or trend of reaction. The following proposal is done for the sake of consideration on such a problem as above and it may be useful to some extent, although the hypothetical treatment has not a restrictly theoretical background.

3.1 Homolytic Decomposition of Organic Compounds

Bond dissociation energies imply the free energy of decomposition of chemical bond, and they may be assumed to be closely related to the activation energies required for the decomposition, and therefore it may be used as a measure of stabilities compounds. From J-e scheme activation energy E_{AB} is expressed as follows:

$$E_{AB}\cong D_{AB}=J_A+J_B-e_Ae_B. \qquad (6)$$

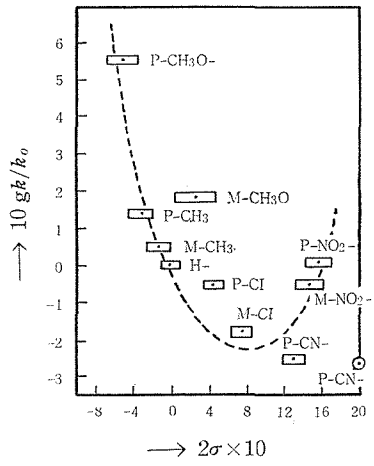
As an example of decomposition we can point out the reaction of substituted benzoyl peroxides, whose decompositions are much easier when the substituents are electron-donating so that the following Hammett's equation (7) holds:

$$\log\ k/k_o=\rho\sigma. \qquad (7)$$

The equation implies that the logarithm of the ratio of rates k for substituted peroxide toward non-substituted one k_o is inversely proportional to the substituent constant. However peroxides with electron-withdrawal substituent such as nitro or cyano group are found by Blomquist[3] to decompose much more easily as is seen in Fig. 1, but mono substituted peroxide does not show such extraordinary effect. This fact may be interpreted in terms of J-e concept. To discuss such substituent effect we can use equation (6), where J terms are supposed not to be affected by polar effect of substituents and hence equation (8) is to be applied.

$$E_{AB}=\text{const}-e_Ae_B \qquad (8)$$

For non substituted benzoyl peroxide, which is a reference compound, equation



A (Blomquist)

Fig. 1.

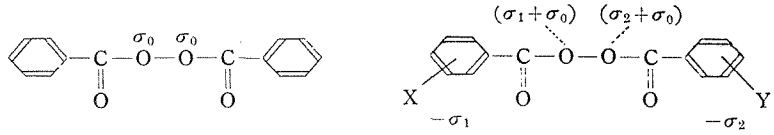
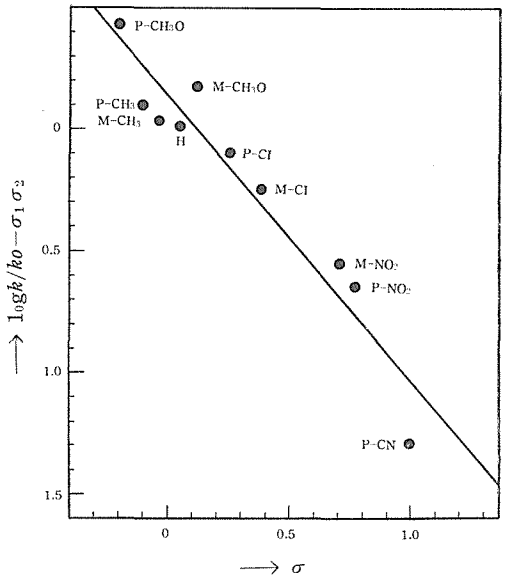


Fig. 2

(9) is derived from equation (8),

$$E_o = \text{const} - \sigma_0 \sigma_0, \qquad (9)$$

where σ_0 is the magnitude corresponding to polarized electron density on oxygen atom of O-O bond. For substituted one the electron density may increase or de-



A′ (Calculated by the author)

Fig. 3.

crease according to the additional effect of substituents denoted by σ_1 and σ_2, and therefore equation (8) should be modified as equation (10) instead of equation (9),

$$E=\text{const}-(\sigma_0+\sigma_1)\ (\sigma_0+\sigma_2). \tag{10}$$

Fig. 2 illustrates the above relation. From equations (9) and (10) it follows that

$$\begin{aligned}\log\ (k/k_0) &= \sigma_0\,\sigma_0-(\sigma_0+\sigma_1)\ (\sigma_0+\sigma_2)\\ &= -\sigma_0(\sigma_1+\sigma_2)-\sigma_1\,\sigma_2.\end{aligned} \tag{11}$$

Equation (11) suggests that the linear correlationship between log $(k/k_0)+\sigma_1\,\sigma_2$ and $(\sigma_1+\sigma_2)$, which is in better agreement with experimental data as is shown in Fig. 3 and from the above relation σ_0 is calculated as -0.3 Hammett's unit.

3.2. Substitution Reaction

For radical type substitutions the discussion is much difficult because the activation energy can not so easily be estimated as decomposition reaction. However it may be said in general that the weaker the bond to be broken and the stronger the bond to be formed is, the lower the activation energy of decomposition will become.

The author proposed the following equation for activation energy of the reaction,

$$\text{AB}+\cdot\text{C} \longrightarrow \text{A}\cdot\cdot\text{B}\cdot\cdot\text{C} \longrightarrow \text{A}\cdot+\text{BC}$$

by assuming linear relation between the activation energy and the effects on bond energy as

$$E=\alpha\ D_{\text{AB}}-\beta\ D_{\text{BC}}, \tag{12}$$

where α and β are constants and they are assumed roughly to be 2/3 and 1/3, respectively. The equation (12) is possibly derived as follows: since activation energy is expressed as

$$E=D_{\text{A}\cdot\cdot\text{B}\cdot\cdot\text{C}}-D_{\text{AB}}, \tag{13}$$

where $D_{\text{A}\cdot\cdot\text{B}\cdot\cdot\text{C}}$ is the bond energy of the transition compound A··B··C. Assuming that

$$D_{\text{A}\cdot\cdot\text{B}\cdot\cdot\text{C}}=\text{a}\ D_{\text{AB}}+\text{b}\ D_{\text{BC}}+\text{c}\ D_{\text{A+B+C}}, \tag{14}$$

it follows that

$$E=(1-\text{a})\,D_{\text{AB}}-\text{b}\ D_{\text{BC}} \tag{15}$$

because $D_{\text{A+B+C}}$ is equal to zero. If a, b and c are equal to 1/3, equation (15) becomes

$$E=2/3\ D_{\text{AB}}-1/3\ D_{\text{BC}}. \tag{16}$$

Combining equations (1) and (15) activation energy is expressed by J-e scheme as follows:

$$E=\{(1-\text{a})J_{\text{A}}+(1-\text{a}-\text{b})\ J_{\text{B}}-\text{b}\,J_{\text{C}}\}-\{(1-\text{a})e_B\,e_{\text{A}}-\text{b}\,e_B\,e_{\text{C}}. \tag{17}$$

This equation affords the substituent effect on the reactivity of compound AB by taking constant J and e values with respect to A and C. And simplified equa-

tion (18) is obtained

$$E = \text{const} + (\text{const}) \times J_B - (\text{const}) \times e_B. \tag{18}$$

In such a way the effect can be ascribed to J_B and e_B, which mean the resonance and polar effect of substituent on component B respectively. From the experiment by Waters[4] on radical substitution of alkyl halide shows that the reactivity is much higher when alkyl group is such as in the following compounds:

Br_3C-Quinolin, $(CH_3)_2C(CN)Br$, $BrC(CH_3)_2COOCH_3$,
$BrCH(COOR)_2$, $CH_2=CHCH_2I$ and $(CH_3)_2C(CN)I$,

where alkyl radicals to be produced are always stabilized due to their conjugated structures and the effect is considered to be ascribed to small J_B values. On the other hand in the competitive oxidation of p-substituted benzaldehydes polar effect on their activities are known to depend actually on the electron-donating ability of substituents as shown in the following order of reactivity[5].

$CH_3O > CH_3 > H > CI > CN$

In this case activation energy varies with e_B values. There are many cases which can be interpreted in terms of J-e concept. The problem whether the effect is positive or negative may be settled by accounting the e_C value. The comparison of reactivity of attacking radical can be made by examining the J_C and e_C values in the following equation:

$$E = \text{const} - \text{b}\, J_C + \text{b}\ e_B e_C. \tag{19}$$

E. C. Kooyman[6] pointed out the reactivity of attacking radicals in substitution in methyl position of toluene was affected by the polarity of the former radical according to the following order,

$C_6H_5N(CH_3)_2 > Br\cdot > Cl_3C.$

In this case hydrogen abstraction of toluene, which is the first step in reaction, is much easier when the attacking radical corresponding to B is positive such as N· and Br·. Here component C corresponding hydrogen atom to be abstracted is highly negative.

3.3. Monomer Reactivity in Co-polymerization

The monomer reactivity in polymerization is one of the problems which were widely studied. Their reactivity ratios can be measured from the co-polymerization data in terms of well-known Mayo-Lewis equation and can be summarized in simple form by the use of Price-Alfrey Q-e scheme, *i. e.*

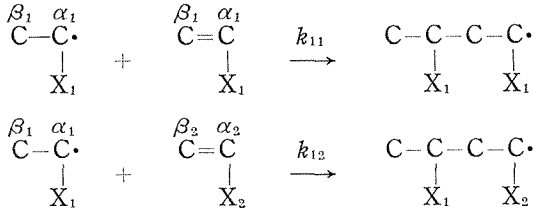
$$r_1/r_2 = Q_1/Q_2 \exp\ e_1(e_1 - e_2), \tag{20}$$

where r, Q and e are monomer reactivity ratio, monomer reactivity due to resonance stabilization in activated state of monomer and polar contribution in substituted monomer, respectively and subscripts 1 and 2 refer to monomer 1 and 2, respectively. Equation (20) can be derived from the following equation representing the rate of propagation,

$$k_{12} \propto P_1 Q_1 \exp(-e_1 e_2), \tag{21}$$

where k_{12} is propagation rate constant of radical-1 toward monomer-2 and P_1 is reactivity of radical-1.

In comparing the following two propagation steps,



the difference between σ- and π-bonds is assumed to be constant and it equals to Δ, then it follows that

$$E_{11}=(1-a)D_{\beta_1\alpha_1}-bD_{\alpha_1\beta_1}-(1-a)\Delta \tag{22}$$

$$E_{12}=(1-a)D_{\beta_1\alpha_2}-dD_{\alpha_1\beta_2}-(1-a)\Delta, \tag{23}$$

where subscripts α and β refer to α-carbon and β-carbon of monomer or radical. If J and e of α-carbon are assumed to be proportional to those of β-carbon, respectively, they are simply written as

$$J_{\alpha 1}=mJ_{\beta}=J_1, \tag{24}$$

$$J_{\alpha 2}=mJ_{\beta 2}=J_2, \tag{25}$$

$$e_{\alpha 2}=ne_{\beta 1}=e_1, \tag{26}$$

$$e_{\alpha 2}=ne_{\beta 2}=e_2. \tag{27}$$

From equations (22)—(27) it follows that:

$$\begin{aligned}2.3\,RT\cdot r_1=RT\,\ln(k_{11}/k_{12})=&[\{(1-a)(1+m)\\&-bm\}J_2-(1-a)n\,e_2^2]-[\{(1-a)(1+m)\\&-b\,m\}J_1-(1-a)n\,e_1^2]-b\,n\,e_1(e_1-e_2).\end{aligned} \tag{28}$$

Equation (28) is composed of three terms, the first of which refers to species 1 alone and the second species 2 alone. The third term represents the product of 1 and 2. Therefore the form of equation (28) can be regarded to be the same as equation (20). However J-value indicates radical reactivity, whereas Q-value does monomer reactivity so that J may be inversely related to Q, although e-value is proportional to e of Q-e scheme. Table 4 affords comparison of both values.

Table 4.

Monomer	e	ln Q	Radicals	e	J
$CH_2=CH_2$	0	0	$CH_3-CH_2\cdot$	0	41.5
$(CH_3)_2C=CH_2$	−1.2	−0.7	$(CH_3)_3C\cdot$	−0.2	30
$(C_6H_5)CH=CH_2$	−0.8	0	$C_6H_5CH_2CH_2\cdot$	0	<32
$ClCH=CH_2$	0	−0.5	$ClCH_2CH_2\cdot$	0	31

IV. SIGNIFICANCE OF J-VALUE OF RADICAL SOURCE

Reagents for radical reaction are usually classified according to their reaction mode into three groups, chain initiator, chain transfer agent and chain stabilizer.

J-e scheme is useful in examination of reactivity of a given reagent. In general radical reaction proceed through chain mechanism, which involves initiation, propagation and termination.

$$\text{(1)}\quad AB \xrightarrow{k_1} A\cdot + B\cdot \qquad \text{(decomposition)}$$

$$\text{(2)}\quad A\cdot + CD \xrightarrow{k_2} AC + D\cdot \qquad \text{(initiation)}$$

$$\text{(3)}\quad D\cdot + BA \xrightarrow{k_3} DB + A\cdot \qquad \text{(propagation)}$$

$$\text{(4)}\quad A\cdot + B\cdot \xrightarrow{k_4} AB \qquad \text{(termination)}$$

Mode of reactivity of reagent can be examined by the ability for initiation, propagation and termination. In other words the reactivity of the radical A is a determinant for the chain length ν of this reaction and the above classification is based on the effect of reagent on chain length, *i. e.* initiator and chain transfer agent afford chemical chain (not polymer chain in polymerization) and stabilizer (inhibitor) does short one Chain length ν is generally expressed by equations (29) and (30)

$$\nu = \frac{k_2}{(k_1 k_3)} \cdot \frac{BC}{AB} \tag{29}$$

and

$$2.3 \log \nu = \text{const} - \frac{1}{RT}\left(E_2 - \frac{1}{2}E_1 - \frac{1}{2}E_3\right), \tag{30}$$

where E_1, E_2 and E_3 are activation heat of corresponding reaction. If they are expressed by using bond energies concerned,

$$\left.\begin{aligned} E_1 &= D_{AB} \\ E_2 &= (1-a)D_{CD} - b\,D_{AC} \\ E_3 &= -D_{AB} \end{aligned}\right\} \tag{31}$$

it follows that

$$2.3 \log \nu = \text{const} - \frac{1}{RT}[(1-a)D_{CD} - b\,D_{AC}] \tag{32}$$

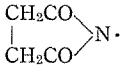
and the effect of reagent AB is given by equation (33),

$$2.3\,RT \log \nu = \text{const} + b\,J_A - b\,e_A e_C. \tag{33}$$

Equaion (33) leads us to the conclusion that chain length ν increases with increasing *J*-value of component A or B involved in the reagent, *i. e.* the reagent consisting of component with large *J*-value can be used as chain transfer agent, while that with small *J*-value acts as terminator, inhibitor or stabilizer. However, if *J*-value is extremely large, it hinders the reaction (3) and acts as initiator but not as propagator. Table 5 summarizes various reagent according to *J*-value of their components.

The action of various radicals on vinyl compounds and natural rubber were studied in our laboratory. In the latter case reagents act as cross-linking agent, peptization agent, inhibitor for vulcanization *etc.* according to the reactivity of radicals, the discussion on which is presented in other papers[7].

Table 5.

	Component	J	e	Reagent for radical source
Initiator	H·	56	−2.8	Hydrogen atom in situ
	C_6H_5·	54	−2	Benzoyl peroxide, diazoaminobenzene
	·OH	46	+6	$H_2O_3+Fe^{++}$
	·NH_2	44	+5.2	H_2NNH_2
	CH_3·, C_2H_5·	42	0	Alkyl peroxide, aliphatic azocompounds
	$CH_3\dot{C}=O$	35	−3.3	Acetone (in light), aldehyde (in light)
Transfer agent	n-C_3H_7·	34	0	Halogenoalkyl
	i-C_3H_7·	34	0	Halogenoalkyl
	·CCl_3	34	?	$HCCl_3$, CCl_4
	·Cl	32	+2	Cl_2
	t-C_4H_9	30	+0.2	Halogenalkyl
	-$CH_2\dot{C}HX$	30—40	0	Vinyl monomer, maleic ester
	CH_3S·	30	0	Mercaptan
	$C_6H_5\dot{C}=O$	30	−2.5	Aromatic ketone
	C_2H_5O·	27	−5	Alcohol
	C_2H_5S·	27	0	Mercaptan
	Br·	25	+0.3	Br_2
	·SO_2Cl	?	?	SO_2Cl_2
	$C_6H_5CH_2$·	23	0	Benzyl chloride, toluene
	CH_2 $CHCH_2$·	20	0	Alkyl chloride, propylene
		~10	+5	N-Bromosuccinic imide
	I·	15	−1	Alkyl iodide, HI
Terminator	·NO_2	12	−1	N_2O_4
	·NO	2	0	N-Nitrosoacetamide, N-nitroso-diphenylamine

V. AN ATTEMPT TO ESTIMATE CHARGE DISRTIBUTION IN COMPLICATED MOLECULE

J-e concept may be more promising if data of *J-e* value are available, but so much data about bond energy are not given enough. Since *e*-value can be calculated from electronegativity as mentioned before, tendencies of polar nature will be estimated from electronegativity. The following discussion concerns the estimation of electronegativity of atoms in complicated compounds.

5.1 Charge Distribution in Polyatomic Molecule

It is more convenient to estimate charge distribution in molecule instead of electronegativity, because the former can be calculated additively even in case of polyatomic molecule unlike the latter.

The polarized charge δ in diatomic molecule A-B was given by Pauling[2], which was expressed by the exponential function of electronegativity of difference atoms

A and B,

$$\delta = 1 - \exp\left\{-\frac{1}{4}(X_A - X_B)^2\right\} \tag{34}$$

and roughly given by equation (35):

$$\delta \cong 4(X_A - X_B)^2. \tag{35}$$

Combining equations (35) and (3) (Pauling's equation) the bond energy is also expressed in terms of charge distribution such as:

$$D_{AB} = (D_{AA} + D_{BB})/2 + (23.06/4). \tag{36}$$

Here δ implies polarized charge in diatomic bond A-B and simultaneously it means charge deviation from the reference state, where the charges are neutralized. Therefore in the case of triatomic molecule whose charge distribution is such that

$$\begin{array}{ccccc} \delta & & -(\delta+\delta') & & \delta' \\ A & \text{——} & B & \text{——} & C. \end{array}$$

The charge distribution after neutralization may be expressed as

$$\begin{array}{ccccccc} \dfrac{\delta-(\delta+\delta')}{2} & & \dfrac{(\delta+\delta')}{2} & & \dfrac{-(\delta+\delta')+\delta'}{2} & & \\ A & \text{——} & B & \text{——} & C & \text{or} & \end{array} \qquad \begin{array}{ccccc} -\dfrac{\delta'}{2} & & \dfrac{(\delta+\delta')}{2} & & -\dfrac{\delta}{2} \\ A & \text{——} & B & \text{——} & C \end{array}$$

and subsequently the charge deviations δ_{AB} and δ_{BC} from neutral state may be expressed as:

$$\delta_{AB} = \delta - \left(-\frac{\delta'}{2}\right) = \delta + \frac{\delta}{2} = \frac{\delta + (\delta' + \delta)}{2}, \tag{37}$$

$$\delta_{BC} = \delta' - \left(-\frac{\delta}{2}\right) = \delta' + \frac{\delta}{2} = \frac{\delta' + (\delta + \delta')}{2}. \tag{38}$$

Inserting equations (37) and (38) into equation (35), the resultant electronegativity of A, B and C triatomic molecule is obtained such that

$$1/4 \times (\delta + \delta' + \delta)/2 = (X_A - X_B)^2 \tag{39}$$

and

$$1/4 \times (\delta' + \delta' + \delta)/2 = (X_B - X_C)^2. \tag{40}$$

Combining equations (39) or (40) and equation (3), it follows that

$$D_{AB} = (D_{AA} + D_{BB})/2 + (c/2)(\delta + \delta' + \delta), \tag{41}$$

$$D_{BC} = (D_{BB} + D_{CC})/2 + (c/2)(\delta + \delta' + \delta), \tag{42}$$

where c is $23.06 \times 1/4$.

5.2. Effect of Polarized Charge on Radical Decomposition

In the radical decomposition of triatomic molecule the energy required can be calculated by analyzing the direct and indirect routes as follows:

$$\begin{array}{ccccccccccc} \delta & & -(\delta+\delta') & & \delta' & \Delta H_1 & & \delta' & \delta & \Delta H_2 & \cdot \\ A & \text{——} & B & \text{——} & C & \longrightarrow & A\cdot + \cdot B - C & & \longrightarrow & & A\cdot + B\cdot + C\cdot \\ \multicolumn{11}{c}{\vert \qquad\qquad\qquad\qquad \Delta H \qquad\qquad\qquad\qquad \uparrow} \end{array}$$

Here heats of decomposition ΔH and ΔH_2 can be expressed by using equation (41) and (42) as

$$\Delta H = [-(1/2)(D_{AA}+D_{BB})-(c/2)(\delta+\delta'+\delta)] + [-(1/2)(D_{BB}+D_{CC})-(c/2)(\delta+\delta'+\delta')] \quad (43)$$

and

$$\Delta H_2 = [-(1/2)(D_{BB}+D_{CC})-c\delta']. \quad (44)$$

From equations (43) and (44), the dissociation heat ΔH_1 for bond A-B is calculated as equation (45),

$$\Delta H_1 = \Delta H - \Delta H_2 = -(1/2)(D_{AA}+D_{BB})-c\{\delta+(\delta+\delta')/2\}. \quad (45)$$

Equation (45) implies that the bond dissociation energy in triatomic molecule is larger than that in diatomic one by $(c/2)(\delta+\delta')$ due to the contribution of neighboring atom C.

Thus it is possible to compare the heat stability of hydroxyl compounds or amines. For example hydroxyl compounds are found to be stable according to the following order

$$HOH > ROH > ROR$$

by the calculation as is shown below.

$$\overset{0.38}{H}\text{—}\overset{-0.76}{O}\text{—}\overset{0.38}{H} \longrightarrow HO\cdot + H\cdot \qquad \Delta H = -(D_{OO}+D_{HH})-(c/2)\times 1.52$$

$$\overset{0.22}{R}\text{—}\overset{-0.60}{O}\text{—}\overset{0.38}{H} \longrightarrow RO\cdot + H\cdot \qquad \Delta H = -(D_{OO}+D_{HH})-(c/2)\times 1.36$$

$$\overset{0.22}{R}\text{—}\overset{-0.44}{O}\text{—}\overset{0.22}{R} \longrightarrow RO\cdot + R\cdot \qquad \Delta H = -(D_{OO}+D_{RR})-(c/2)\times 0.88$$

Here charge distribution or ionic fraction of bonds O-H and O-R are referred from Pauling's data or can be calculated by using equation (34). Similarly in the case of amines, it follows that

$$NH_3 > RNH_2 > R_2NH$$

$$\begin{array}{l} \overset{0.17}{H}\text{—}\overset{-0.51}{N}\text{—}\overset{0.17}{H} \\ \qquad\quad | \\ \qquad\quad \underset{0.17}{H} \end{array} \longrightarrow NH_2\cdot + H\cdot \qquad \Delta H = -(D_{NN}+D_{HH})-(c/2)\times 1.02$$

$$\begin{array}{l} \overset{0.05}{R}\text{—}\overset{-0.345}{N}\text{—}\overset{0.17}{H} \\ \qquad\quad | \\ \qquad\quad H \end{array} \longrightarrow R_2N\cdot + H\cdot \qquad \Delta H = -(D_{NN}+D_{HH})-(c/2)\times 0.78$$

etc.

5. 3. Effect of Polarized Charge on Ionic Decomposition

In such an ionic decomposition as

$$\overset{\delta+}{A}-\overset{\delta-}{B} \xrightarrow{\Delta H_1} A\cdot + B\cdot \xrightarrow{\Delta H_2} A^+ + B^-$$

$$\Delta H$$

decomposition heat ΔH can be calculated similarly to the preceding paragraph, considering additional terms I_A and A_B, which are ionic potential for A and electron affinity for B respectively, and it follows that:

$$\Delta H=\Delta H_1+\Delta H_2=-(1/2)(D_{AA}+D_{BB})-c\delta-I_A+A_B. \tag{46}$$

5.4. Formation of Complex Ion and its Ionic Decomposition

Heat of protonation of alcoholic derivatives or amines is possibly calculated as follows:

$$H^+ + \overset{\delta_1}{R_1} - \overset{-(\delta_1+\delta_2)}{O} - \overset{\delta_2}{R_2} \longrightarrow \left[\overset{\delta_1}{R_1} - \overset{1+(\delta_1+\delta_2+\delta_H)}{O} - \overset{\delta_2}{R_2}\right]^+ \quad (H\ \text{on O, charge}\ \delta_H)$$

$$H-O-H+H^+ \longrightarrow H-\overset{-0.14}{O^+}(H)-\overset{0.38}{H} \qquad \Delta H=-(I_O-I_H)+\frac{c}{2}\times 0.5+\text{const.}$$

$$R-O-H+H^+ \longrightarrow R-\overset{-0.02}{O^+}(H)-\overset{0.38}{H} \qquad \Delta H=-(I_O-I_H)-\frac{c}{2}\times 0.72+\text{const.}$$

$$R-O-R+H^+ \longrightarrow R-\overset{0.18}{O^+}(H)-R \quad (0.38) \qquad \Delta H=-(I_O-I_H)-\frac{c}{2}\times 1.04+\text{const.}$$

$$\left(\text{const.}=\frac{1}{2}(D_{OO}+D_{HH})\right)$$

$$H-\overset{-0.51}{N}(H)-\overset{0.17}{H}+H^+ \longrightarrow H-\overset{0.32}{N^+}(H)-\overset{0.17}{H} \qquad \Delta H=-(I_N-I_H)-\frac{c}{2}1.44$$

$$R-\overset{0.05}{N}(H)-\overset{-0.345}{H}+H^+ \longrightarrow R-\overset{0.44}{N^+}(H)-\overset{0.17}{H} \qquad \Delta H=-(I_N+I_H)-\frac{c}{2}0.66$$

$$R-\overset{-0.27}{N}(H)-R+H^+ \longrightarrow R-\overset{0.56}{N^+}(H)-R \qquad \Delta H\equiv-(I_N+I_H)+\frac{c}{2}0.72$$

$$R-\overset{-0.15}{N}(R)-R+H^+ \longrightarrow R-\overset{0.68}{N^+}(R)-R \qquad \Delta H=-(I_N+I_H)+\frac{c}{2}[1.50].$$

In these calculations the charge on protonated oxygen atom *i.e.* oxonium ion is expressed as $1+\Sigma\delta$, where δ is polarized charge induced by neighboring group and

l means ionic charge induced by protonation.

As a result protonation tendences *i. e.* proton affinities of alcoholic derivatives and amines may be predicted as follows:

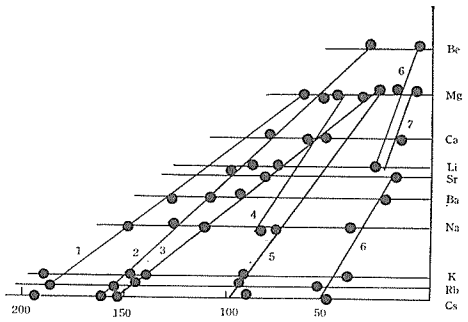
$$H_2O > ROH > ROR$$

$$\underset{(4.75)}{NH_3} < \underset{(3.37)}{RNH_2} > \underset{(3.22)}{R_2NH} < \underset{(4.20)}{R_3N}$$

Figures in parenthesis are observed values of pK_b in literature.

5.5. Acidity of Anion and Basicity of Cation on Salt Formation

It has been known that heat of formation is expressed as a linear function of basicity of cation as is shown in Fig. 4. For example heat of formation of potassium



$-\Delta H$ (Kcal) ←

Fig. 4.

1. ClO_4 2. SO_4 3. NO_3 4. PO_4 5. CO_3 6. OH 7. SiO_4

perchlorate is expressed as

$$K^+ + ClO_4^- \longrightarrow KClO_4 + \Delta H$$

$$\Delta H = c + b_{(ClO_4)} \times Z_{(K)}$$

where b and Z are specific values for perchlorate ion and potassium cation, respectively. In other compounds b and Z are shown in Table 6.

Table 6.

	ClO_4^-	NO_3^-	SO_4^{--}	PO_4^{--}	CO_3^{--}	OH^-	SiO_3^{4-}
b	29	28.2	24	24	16.7	12.5	7.5

	Cs^+	Rb^+	K^+	Na^+	Ba^{++}	Sr^{++}	Li^+	Ca^{++}	Mg^{++}	Be^{++}
Z	8.2	8.0	7.7	6.5	6.0	5.5	5.3	4.8	3.7	2.7

It is of interest to find that b tends to increase with increasing of net charge of oxygen atom in anion while Z decreases with increasing electronegativity of in cation as shown in the Figures 5 and 6 shown below.

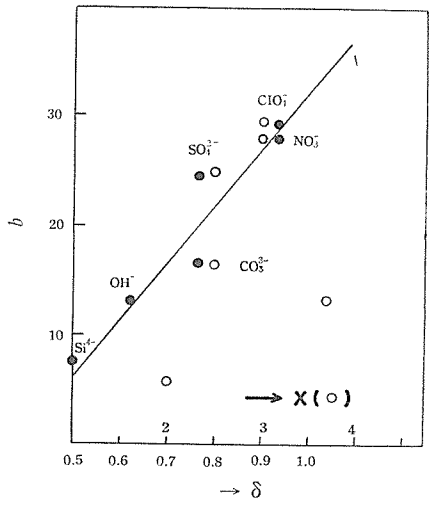


Fig 5.

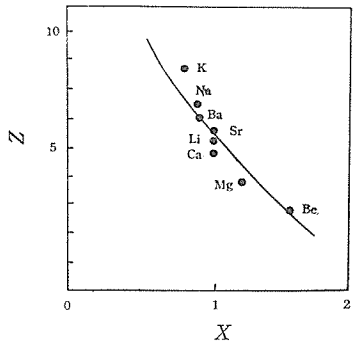


Fig. 6.

5.6. Polarized Electron Density in Ziegler Type Catalysts

Ziegler type catalysts consist of two components, one is metal alkyl and the other is compounds of transition metal. Although the mechanism of the catalytic action of this type catalyst is still remained unsettled, complex compounds of two components, which are combined by electron deficient bond, seem to play a great role. For example, in Fig. 7, electron pair on anionic polymer terminal tends to transfer to neighboring olefin, which is chemisorbed on titanium atom and simultanous charge transfer from titanium to aluminum is followed. In the second step

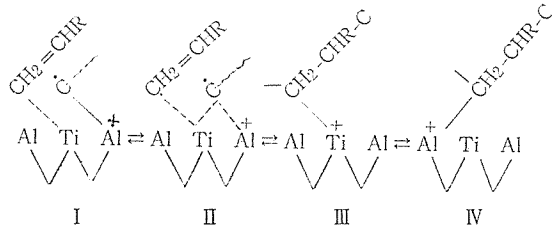
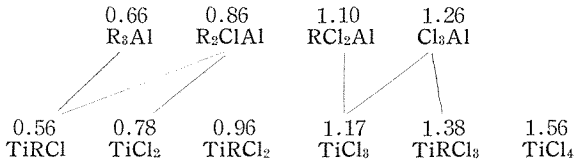


Fig. 7.

of propagation carbanion on titanium atom will migrate to aluminum. Repeating of such process enables to induce propagation. Thus polymerization is considered as a kind of interchange reaction between aluminum and titanium atom.

According to this process it is easily concluded that in order to make polymerization easily bonding natures of both components against carbanion should not be appart from each other and, in other words, both elements in catalyst complex are as similar as possible to each other in covalent and polar property. The following Table 7 indicates electron density of aluminum and titanium in various types of related compounds. From this point of view there are a few suitable pairs indicated by the connection lines.

Table 7.



Comparison of calculation with experimental result seems to suggest the validity of the hypothesis.

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